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Nitrate Removal by Catalytic Reduction in Water in the Presence of a Pd-In/Tio_2 Catalyst and Formic Acid as a Reducing Agent

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ABSTRACT

Catalytic reduction is one of the methods used for the removal of nitrates from polluted water. The aim of the present study was to define the appropriate method for the catalyst preparation as well as the operating conditions that could maximize the activity of the catalyst for the reduction of nitrates and minimize the percent of ammonium formed. A 5% Pd-1.75% In/TiO_2 bimetallic catalyst was chosen in order to define these parameters. The catalyst was characterized by Scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction. It comes out from the results that, the apparent activation energy is 44,8kj/mol obtained; the initial concentration used to produce carbon dioxide and hydrogen of formic acid is 16 mmol/L and this enable us to obtain the best activity as well as the weakest selectivity of ammonium ion.

1. INTRODUCTION

Groundwater pollution by harmful nitrogen containing compounds is a growing environmental problem. Nitrates consumed in drinking water can be converted in human body and may cause health problem. The concentration level of nitrate acceptable in water by European Union and World Health Organization is 50ppm (USEPA, 1995). Nitrate in groundwater comes from different sources as natural; waste materials; row crop agriculture and irrigated agriculture Canter *et al.,* (1997).

Biological and physicochemical treatments allow effective removal of nitrates but have several economical and ecological disadvantages. Catalytic reactions constitute promising approaches for the destruction of pollutants in water. Since the first paper of Tacke *et al.,* (1989) on the use of palladium-copper bimetallic catalysts for nitrate reduction, numbers of studies have been aimed at the development of suitable catalysts for the selectivity reduction of nitrogen gas. Tacke *et al.,* (1989); Epron *et al.,* **(**2001); Wärna *et al.,* **(**1994); Hählein *et al.,* (1998); Daub *et al*., (1999). In particular, noble metals including Pt, Pd, and Au have always attracted significant attention owing to their broad applications Sahu *et al*., (2013); Chen *et al* (2010), especially in catalysis Zhou *et al*., (2012); Si *et al*., (2013).

Nitrate reduction for drinking water treatment needs active catalysts since the reaction has to be performed at the temperature of the groundwater. Moreover, a high selectivity is necessary to avoid the production of ammonium ions by over reduction of intermediates by the stepwise nitrate hydrogenation. This selectivity is directly controlled by hydrogen coverage of the precious metal.

The reduction of nitrate leads to the formation of hydroxide ion that causes an unavoidable increase in the pH value up to 10, which is unacceptable in drinking water. Furthermore, the presence of hydroxide induces a polarization of the support and has a repulsive effect on nitrate and nitrite, inducing a decrease in the activity and the selectivity to nitrogen Pintar *et al.,* (1998).

Different solutions have been used to reduce the formation of hydroxide Pintar *et al*., (1998); Vorlop *et al*., Pintar *et al*., (1998); Pintar *et al*., (2001); Gautron *et al*., **(**2003); Roveda *et al*.,(2003); Gavagnin *et al*., (2002). The use of formic acid (FA) instead of hydrogen as reducing agent is one possibility Pintar *et al*., (2001); Gautron *et al*., **(**2003); Roveda *et al*.,(2003); Gavagnin *et al*., (2002); D'Arino *et al*., (2004).

In this case, the Formic acid (FA) decomposition can be used as a source of hydrogen and carbon dioxide, which may neutralize the hydroxide ion produced during nitrate reduction and thus can help to maintain an acidic pH.

Indeed, on a noble metal FA can be easily decomposed according to the following reaction:

$$HCOOH \longrightarrow H_2 + CO_2$$

The aim of the present study is to determine the best reaction conditions for selectively reducing nitrate into nitrogen using a bimetallic Pd-In catalyst supported on Titania oxide.

Thus, how to determine such appropriate reaction conditions is the key to minimizing the effectiveness of catalytic nitrate reduction. In this aspect, few studies have been systematically conducted. Therefore, the focus of this study is to investigate the appropriate reaction conditions (Temperature, initial concentration of formic acid, appropriate gas such as either N_2 or H_2) and the catalyst composition.

2. MATERIAL AND METHODS

2.1. Catalyst Preparation

2.1.1. Catalyst Preparation by Catalytic Reduction.

a) Monometallic Catalyst

A powered Titiana from pro catalyst surface area (BET) method, 32 m^3/g; pore volume 0.24 cm^3/g has been used as support the particle sizes is 32nm. Monometallic catalyst was prepared by an impregnation method using aqueous solutions of precursor salts $PdCl_2$ This step consisted salts and Titania surface; after evaporation of water, catalysts were dried at 100°C, calcinated by flowing hydrogen at 300°C. Monometallic catalysts Pd/TiO_2 had a metal loading of 5w%.

b) Bimetallic Catalysts

Bimetallic catalysts were prepared by a controlled surface reaction. In order to obtain great metal-metal interactions; the second metal was deposited by a redox reaction occurring between the hydrogen adsorbed on the pre-reduced noble metal and the oxidized modifier. A known amount of a monometallic catalyst was placed in an atmospheric glass reactor.

The reactor was flushed with counter current nitrogen flow for 15 min at room temperature afterward the catalyst was reduced by a hydrogen stream at a temperature rising to 300°C and then cooled to room temperature. At the same time, the desired amount of the modifier was pre-dissolved in water and degassed by bubbling with N_2. The solution was then added to the monometallic catalyst and maintained under stirring by hydrogen flow (mL/min) for 2h. The bimetallic catalyst was separated from the aqueous solution via a filter in the bottom of the reactor and washed. Afterward, the resulting material was dried overnight under of hydrogen stream at 100°C.

2-1-2- Preparation of Catalyst by Co-impregnation (CI)

The co-impregnation consists in immersing a quantity of the Titania in ultra pure water and adding the necessary amounts of both $PdCl_2$ and In $(NO_3)_3$ precursor salts. The reaction mixture was stirred during 3h before being evaporated on sand bath and dried in an oven during a night (100°C)

2-1-3- Preparation of Catalyst by Code position precipitation

Titania was suspended in a 2% Na_2CO_3 solution, for fifteen minutes, under magnetic agitation. Palladium salt($PdCl_2$) and Indium salt $(In(NO_3)_3$ were then added dropwise while maintaining and efficient agitation a contact time of two hours was applied in order to completely precipitated the metallic salts at the surface of Titania.

Lastly, the solution was allowed to stir overnight after which the metals were reduced by adding a 20% formic acid solution. At the end, the aqueous suspension was evaporated in a sand bath at 100°C, then placed in an oven for one night, in order to obtain a dry powder.

The powder collected was then calcinated for 4 hours at a temperature of 400°C followed by a 2 hours temperature reduction to 300°C.

2.2. Catalyst Test Evaluation

Nitrate reduction reaction was performed in a semi-batch reactor, at atmospheric pressure and 298K. The catalyst (64mg) is first reduced once again under hydrogen (373K, 1h, pH_2 = 1bar, flow rate = 250mL/min). Meanwhile, 80mL of ultrapure water are placed in a vial purged with nitrogen and added 10 mL of formic acid are placed in a vial purged with nitrogen. The mixture of water and formic acid was introduced into the reactor for 1 h.

Afterward, 10 mL of a solution (16 mmol/L) of potassium nitrate (KNO_3) were introduced into the reactor to start the reaction. The catalyst dispersion in the medium was achieved by the gas flowing (flow rate = 250 mL/min^{-1}) through a porous glass located at the bottom of the reactor.

It was checked that the gas flow and resulting stirring were sufficient to ensure that the reaction, the representative aqueous samples were periodically drawn and immediately separated by filtration and then analyzed by High-Performance Liquid Chromatography (HPLC), in order to determine the NO_3^-, NO_2^- and NH_4^+ concentrations.

Nitrate concentrations were determined after separation at 40°C on a Zorbax Eclipse XDB-C18 column using a UV detector at $\lambda = 210$ nm. Ammonium ions were quantified using an Alltech Universal cation column at 30°C coupled with a conductivity (oxalic acid) used provided the complete conversion of the ammonia basic form into ammonium ions.

2.3. Catalyst Characterization

2.3.1. X-Ray Diffraction (XRD)

Low angle XRD patterns were obtained using a Rigaku X-ray diffractometer (Rigaku model) apparatus with a CuKα radiation at 30mA and 40 kV. Also, wide-angle measurements (ca. $2\theta = 3$–80°C) were recorded on the same equipment.

2.3.2. Scanning electron microscopy (SEM)

SEM measurements were conducted on a JEOL JEM-2010 electron microscope equipped with an EDX Link Analytical QX-20000 system coupled to the SEM microscope, using an acceleration voltage of 200 kV.

2.3.3. Raman spectroscopy

Raman spectra of the selected spent catalysts were obtained on a T64000 Raman spectrometer (JobinYvon triple spectrometer) under ambient conditions. A 514.5nm Ar laser was used as the exciting source on the sample surface and a power of 20mW. The measurements were referenced to Si at 521cm^{-1} with 16 data acquisitions in 120 s. The lens focus was of 100 times.

3. RESULT AND DISCUSSION

3.1. Characterization of the Bimetallic Catalysts

3.1.1. XRD

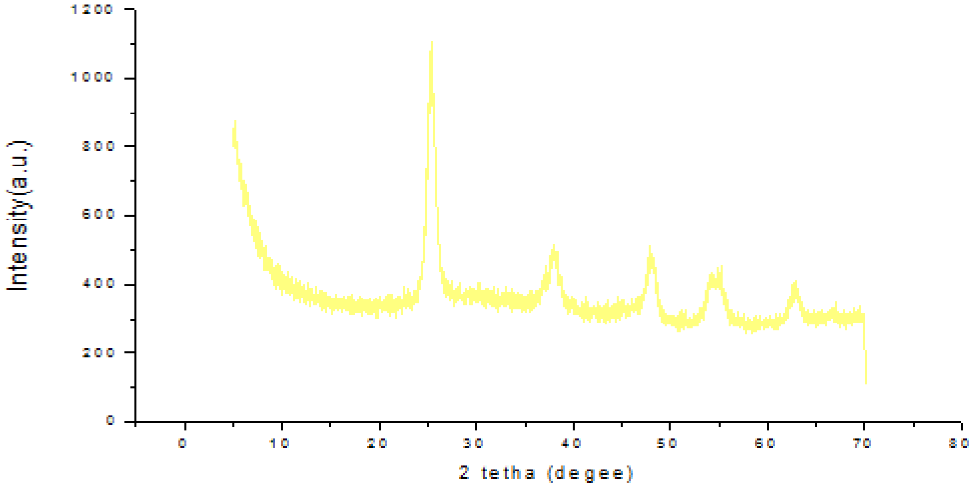

Fig. 1. *XRD Pattern of Pd-In/*TiO_2

Fig.1 show the XRD pattern of the catalyst Pd-In/TiO_2.The XRD profile was magnified between 5◦ and 70°. XRD pattern of TiO_2 corresponds well with the reflections of a tetragonal rutile phase with 2θ values of 25.3, 36.6, 48.0, 54.5 and 62.6°, which can be indexed to the (101), (004), (003), (105) and (204) planes of cubic anatase, respectively and in agreement with JCPDS 21-1272. Were not detected for samples with Pd or in addition, suggesting that the surface in species on this catalyst be either amorphous structure or highly dispersed.

3.1.2. Raman spectroscopy

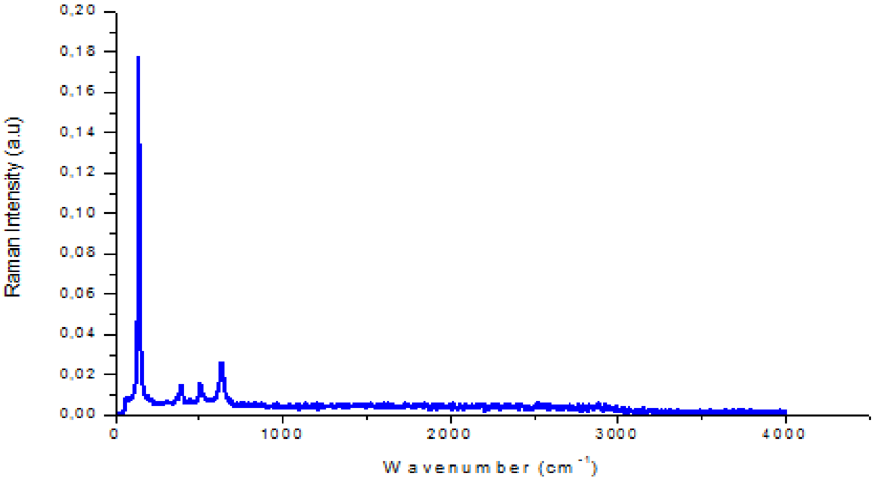

Fig.2: *Raman spectra of the catalyst Pd-In/*TiO_2

A Raman spectrum of the synthesized Pd-In/TiO_2 sample is given in **Fig.2.** The Raman lines at 144, 397, 516 and 640 cm^{-1} can be assigned as the Eg, B1g, A1g + B_{1g}, and Eg modes of the anatase phase, respectively. The strongest Eg mode at 144 cm^{-1} arising from the external vibration of the anatase structure is well resolved, which indicates that an anatase phase was formed in the as-prepared nanocrystals and long-range order was somewhat formed.

3.1.2. Scanning Electron Microscopy (SEM)

Following their preparation, the three samples were observed by SEM. **Fig. 3** (A, B, C) respectively show the micrographs obtained for catalysts prepared by co-impregnation, precipitation and by catalytic reduction. Recall that for the catalysts prepared by co-impregnation and by precipitation, indium is more likely to deposit on the surface of titanium dioxide, because these methods lead random deposition of metals (co-impregnation) or indium (precipitation), whereas the catalytic reduction promotes indium deposition at the surface of the palladium. Note that in this case the deposition of indium titanium dioxide is limited because deposition of indium palladium is faster. We can, therefore, assume that the catalytic reduction helps achieve bimetallic palladium-indium entities without preventing the indium deposit on the support.

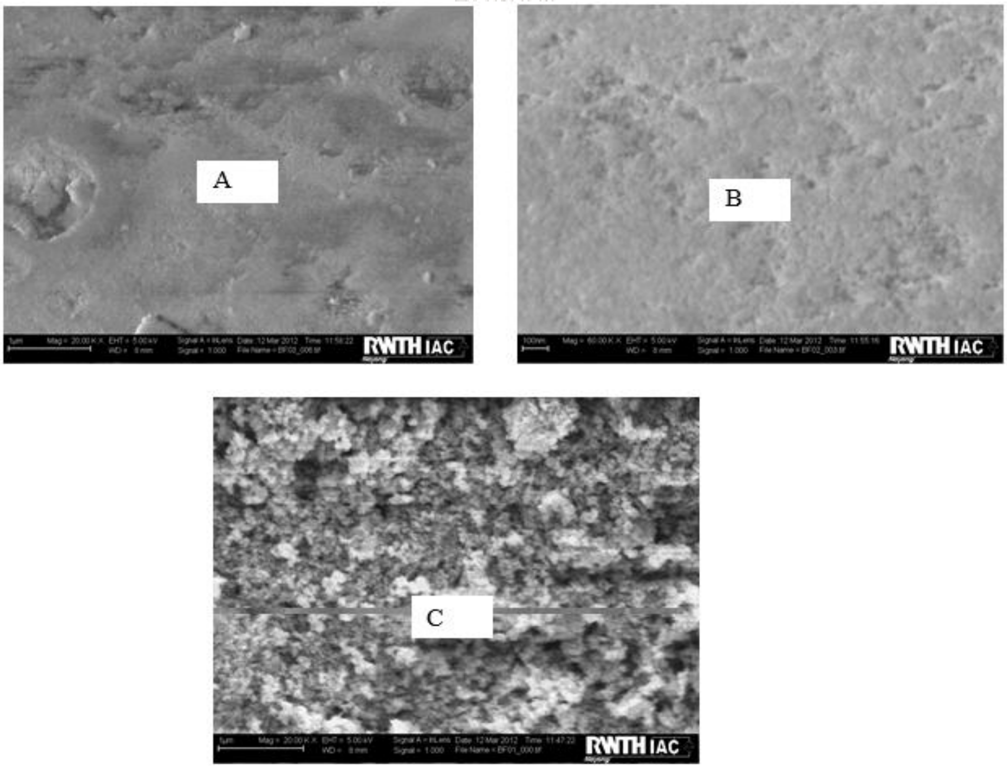

Figure 3: SEM image: co-impregnation (A), precipitation (B) and catalytic reduction(C).

The SEM image obtained at low magnification does not distinguish between the metal particles. The micrograph of the catalyst prepared by catalytic reduction suggests a different texture. Overall, these three catalysts have different morphologies; this could lead to differences in catalytic behavior observed above in the catalytic reduction of nitrates.

3.2. Influence of preparation method of catalyst

The preparation method of the catalyst plays an essential role in the activity and selectivity of the catalyst. In order to compare the performance of different methods for the reduction of nitrates, we have carried out a study on the catalyst 5%Pd-1.75%In/TiO2, using the following methods: catalytic reduction; co-impregnation and code position-precipitation. The resultants obtained during the reduction of nitrates as function of the preparation method are presented in table 1.

If come out from the results obtained that the activity and selectivity, as a function of the preparation mode, can be classified in the following order:

Activity: Catalytic Reduction (CR) > Co-impregnation (CI) > code position-precipitation(CD).

Selectivity: Catalytic Reduction (CR) > Co-impregnation (CI) > code position- precipitation (CD).

This difference of activity and selectivity could be attributed to the difference in morphology of the catalyst. In fact, catalytic reduction leads to a controlled deposition of Indium in interaction with palladium. Whereas the code position-precipitation and co-impregnation methods rather give a random deposit of the metals at the surface of Titania.

The metal separation thus obtained are effectively distinct in both cases; that’s why they could generate the formation of bimetallic entities of different composition and in variable quantities with respect to the method chosen for the sample preparation. One of these phenomena could justify the observation of a great activity for the sample prepared by catalytic reduction.

On the other hand, we notice that the weakest, as well as the most important selectivity in ammonium ion, are obtained by code position precipitation method. This could be explained by the disactivation of the sites responsible for the elimination of nitrates, notably the sites of Indium.

This mechanism could be the result of many phenomena: an important poisoning of active sites either by intermediate nitrates strongly absorbed at the surface of the catalyst; either by hydroxide ions at the proximity of active site, thus creating repulsive forces vis a vis of nitrates and thus hindering their adsorption.

Table 1: Effect of preparation method of catalysts on their performance in nitrate reduction ([HCOOH] = 8mmol/L, T= 25°C, N_2)

Catalyst	Preparation method	Activity (mmol.min^{-1}.g_{cat}^{-1})	Selectivity (%)	Time(min)	Percent of conversion **(%)**
5%Pd1,75%In/TiO_2	Catalytic Reduction	0,0422	5,22	60	100
	Co-impregnation	0,0076	13,12	330	100
	Precipitation	0,0017	22,66	480	32,87

3.3. Influence of Temperature on the Reaction

The influence of reaction temperature on nitrate reduction over 5% Pd-1.75% In/TiO_2 catalyst was investigated at different temperatures (10, 20, 30°C); table 3 under the given reaction conditions. It was shown that nitrate conversion was logically proportional to the reaction temperature. Higher nitrate conversion was achieved at higher reaction temperature.

Table 2: Properties of bimetallic catalyst vis a vis of the nitrate reduction in function of temperature**.**

Catalyst	Temperature (°C)	Initial Activity A_0 (µmol.min^{-1}.g$_{cat}^{-1}$)	Global Activity A (mmol.min^{-1}.g$_{cat}^{-1}$)	Ammonium Selectivity (%)	Time of reaction (min)	Percent of conversion (%)
5%Pd-1,75%In/TiO_2	10	0,1211	0,0278	7,78	80	100
	20	0,1611	0,0319	9,68	70	100
	30	0,2055	0,0427	8,45	50	100

The apparent activation energy of this reaction, calculated from the initial activity, is equal to 44.8 kJ mol^{-1}. This value, higher than the activation energy of a diffusion process (of the order of 12 to 22 kJ/mol), confirms that a chemical reaction in kinetically dominant. This activation energy is in the same range as the one obtained by Palomares *et al*., **(**2004) (47 kJ/mol) on 1.4%Cu-4.7%Pd/Al_2O_3 bimetallic catalyst, prepared by successive impregnation higher than others reported by Prüsse *et al*.,(2001) (37kJ/mol) on a 0.75%Pt 0.25%Cu/Al_2O_3 bimetallic catalyst prepared by catalytic reduction and by (31 kJ/mol) on a 5%Rh-1.5%Cu/Al_2O_3 bimetallic catalyst prepared by co-impregnation Pledran-Pineda *et al* (1999).

3.4. Influence of the Initial Concentration of Formic Acid

In order to evaluate the influence of the initial concentration of formic acid in the reaction of nitrates, a study at different initial concentrations (1.6, 3.2, 4, 8, 16, 32 mmol/L) of formic acid was carried out. The activity and the selectivity in ammonium ions obtained during the reduction of nitrates in these various conditions are reported in Table 3.

Table 3. Effect of initial concentration of F. A on the performances of 5%Pd-1.75%In/TiO_2 bimetallic catalyst prepared by catalytic reduction (at 100% of nitrate conversion). (Reaction temperature: 20ºC, under N_2)

Initial concentration of F. A (mmol/L)	Activity 10^{-5}mol.min^{-1}g$_{cat}^{-1}$	Selectivity toward NH_4^+ (%)	Final pH
1.6	2.11	5.99	5.91
4	2.61	5.87	5.38
8	4.22	5.26	3.15
16	3.10	0.71	2.73
32	2.06	0.48	2.63

From this study, it can be seen that when a number of FA increases, the final pH decreases, with a direct effect on the selectivity towards ammonium ions. In accordance with the literature, the lower the pH value, the lower the selectivity to NH_4^+. So if the pH value is below 3, as obtained for an initial concentration of FA higher than 8 mmol/L, the selectivity to the desired the product (N_2) will be roughly of 100%. However, for the highest initial concentration of formic acid (32 mmol/L), the conversion of FA is not complete at the end of the reaction, in accordance with Garron *et al*., (2005). As far as the activity is concerned, it is optimal for an intermediate amount of F.A. (8 mmol/L). One can note that the performances of the Pd-In/TiO_2 catalyst are higher than that of the Pd-Sn/SiO_2 studied by Garron *et al*.,(2005), in the same experimental conditions, with a maximal activity of 4.22 10^{-5} mol.min^{-1}g$_{cat}^{-1}$ against 2.99 mol.min^{-1}g$_{cat}^{-1}$ for the Pd-Sn catalyst, and a selectivity to N_2 of nearly 100%, against roughly 95%.

3.5. Influence of the Gaseous Phase

The effect of the gaseous phase on the reduction of nitrates was examined in presence of 5%Pd-1.75%In/TiO_2 bimetallic catalyst and of three gasses: hydrogen, nitrogen, and carbon dioxide, with an initial concentration of formic acid of 16 mmol/L. The results obtained during the reduction of nitrates are presented in table 4.

Table 4. Catalytic performance for nitrate reduction of 5%Pd-1.75%In/TiO_2 catalyst with formic acid (16 mmol/L) as a function of the gasses (at 100% of nitrates conversion)

Gas	Activity 10^{-5}mol.$min^{-1}g_{cat}^{-1}$	Selectivity toward NH_4^+ (%)	Final pH
N_2	3.10	0.71	2.73
H_2	16.55	1.88	3.01
CO_2	0.60	14.61	5.03

It comes out from this table that the most important activity is obtained in the presence of hydrogen gas. This activity is five times more important in the presence of hydrogen than in presence of nitrogen.

This is in accordance with the results obtained by Prüsse *et al.*, (2001) which showed that the addition of hydrogen to the FA and nitrate solution enhances the activity of the catalyst. This was explained by Prüsse *et al.*, (2001) by the fact that FA is only adsorbed, in the form of format, on monometallic palladium sites, where they can directly react with nitrate by a direct redox process, i.e. without decomposition, with nitrate chemisorbed on bimetallic sites. Consequently, the reaction between formate species and nitrate occurs at the interface between the monometallic and the bimetallic entities. The reaction between nitrate and hydrogen is easier since hydrogen, chemisorbed on monometallic palladium site can spill over the bimetallic entities to react with nitrate species.

It is important that contrary to the results obtained by Pintar *et al.*, (1998), there is no induction period at the beginning of the nitrate reduction in presence of FA. The difference could be explained by the way the FA was added. Indeed, in the present study, the total amount of FA is introduced before nitrate while in the study of Vorlop *et al.*, (1999). FA is progressively added during the reaction in order to stabilize the pH at a value of 6. Moreover, theses authors deduced from their experimental curve, a zero-order kinetic with regard to nitrate.

However, it seems that the linear concentration/time could also be attributable to the decomposition kinetic of FA which could limit the nitrate reduction rate Garron *et al*.,(2005) Witonska *et al*.,(2007)., Wehbe et al.,(2009).

5. CONCLUSION

In this work, the effect of the reaction conditions on the performances of a Pd-In/TiO_2 catalysts were studied. Appropriate reaction conditions in order to determine the activity of catalyst and minimize the selectivity of ammonium ion. It was shown that Pd-In/TiO_2 is a very efficient catalyst for removing nitrate from water by catalytic reduction in presence of formic acid. Its activity is high and more important, a selectivity to NH_4^+ close to zero, and consequently a selectivity to nitrogen roughly equal to 100% can be reached.

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